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INFORMATION REPORT

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Soviet Research by Pudovik on New Reactions in
Organophosphorous Compounds

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SUPP. TO
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1. The following information is extracted from quite a large collection of material that became available only a short time ago (early 1953) and the entire stack of articles was published in one journal on the occasion of the seventy-fifth anniversary of Professor A E Arbusov's birth. While each paper represents a legitimate continuation of the author's previous study of phosphorous compounds, [REDACTED] the following specific comments are warranted from the standpoints of interest and significance.
2. A N Pudovik of the A E Arbusov Chemical Institute at Kazan and associates have published six recent articles on new reactions in organophosphorous compounds. The first two discuss a new reaction which is quite interesting from the viewpoint of chemists. While the work falls in line with Pudovik's earlier studies and while it is somewhat doubtful that the compounds he reports are of use as warfare agents, nevertheless any new substances such as these can conceivably be used as warfare agents, and are therefore worthy of noting even though their warfare use is only conjecture.
3. The next two articles are direct continuations of older work and there is better probability that the compounds described therein might be poisonous, although not on a scale that would make them war gasses or products.
4. The last two articles are legitimate continuations of previous work and have no particular significance.
- 25X1 5. For whatever it may be worth, [REDACTED] translated and digested these six articles as follows:
- (a) New method of synthesis of esters of phosphonic and thiophosphonic acids.
Addition of dialkyl phosphites to unsaturated dibasic acids and esters, by A N

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Pudovik of the A E Arbuzov Chem Inst at Kazan, published in Izvest Akad Nauk SSSR, Otdel Khim Nauk, 926-31 (1952).

To 4.2 g maleic acid and 8 g $(\text{MeO})_2\text{POH}$ was added some 10 drops of satd MeONa in abs MeOH, causing an exothermic reaction; distn gave 4.1 g $\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})\text{PO}(\text{OMe})_2$, $b_3^{141^\circ}$, $n_D^{20} 1.4428$, $d_4^{20} 1.2695$, (50%). Similarly, $(\text{EtO})_2\text{POH}$ with EtONa-EtOH catalyst gave 70.8% di-Et analog, $b_1^{137-8^\circ}$, $n_D^{20} 1.4408$, $d_4^{20} 1.1782$. Maleic anhydride (8 g) and 12 g $(\text{MeO})_2\text{POH}$ heated on steam bath and treated dropwise with unstated amount of MeONa-MeOH also gave an exothermic reaction, however on attempted distn the product suffered decompn; similar result was encountered with $(\text{EtO})_2\text{POH}$. To 7.2 g di-Me maleate and 6 g $(\text{MeO})_2\text{POH}$ was added 20 drops satd MeONa-MeOH with cooling (the temp rise to 70° was observed) and after 1 hr on a steam bath the mixture yielded 9.9 g (78%) $\text{MeO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{Me})\text{PO}(\text{OMe})_2$, $b_2^{142^\circ}$, $n_D^{20} 1.4435$, $d_4^{20} 1.2076$. Similarly $(\text{EtO})_2\text{POH}$ with EtONa-EtOH catalyst gave 81.9% $\text{MeO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{Me})\text{PO}(\text{OEt})_2$, ^(I) $b_3^{184^\circ}$, $n_D^{20} 1.4422$, $d_4^{20} 1.1803$, while $(\text{BuO})_2\text{POH}$ similarly gave the di-Bu ester analog, 69.7%, $b_1^{161-2^\circ}$, $n_D^{20} 1.4425$, $d_4^{20} 1.0666$. Heating 3.5 g I with 1:1 HCl in sealed tube 6 hrs at $120-30^\circ$ followed by evapn gave sirupy free acid. Reaction of 6.8 g di-Et fumarate with 6.5 g $(\text{EtO})_2\text{POH}$ in presence of EtONa-EtOH gave 10.2 g (82.3%) $\text{EtO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{Et})\text{PO}(\text{OEt})_2$, $b_2^{161-2^\circ}$, $n_D^{20} 1.4410$, $d_4^{20} 1.1333$; similarly $(\text{BuO})_2\text{POH}$ gave 95.7% di-Bu ester analog, $b_2^{178-9^\circ}$, $n_D^{20} 1.4417$, $d_4^{20} 1.0673$. Addn of few drops satd EtONa-EtOH to 5.6 g $\text{EtO}_2\text{CC!CCO}_2\text{Et}$ and 9.2 g $(\text{EtO})_2\text{POH}$ caused no heat evolution, but continued addn caused a vigorous reaction; distn gave 6 g $[\text{CH}(\text{CO}_2\text{Et})(\text{PO}(\text{OEt})_2)]_2$, (II), $b_2^{213-14^\circ}$, $n_D^{20} 1.4700$, $d_4^{20} 1.3753$. Heating 7 g $\text{EtO}_2\text{CC!CCO}_2\text{Et}$, 5.8 g $(\text{EtO})_2\text{POH}$, 20 ml EtOH and 1 ml satd EtONa-EtOH on steam bath 3 hrs gave 2.7 g II and 5 g product, $b_8^{125-85^\circ}$; redistn gave a fraction, $b_3^{160-3^\circ}$, contg 9.1% F, which indicated the addn of 1 mole $(\text{EtO})_2\text{POH}$ to the triple link. Addn of M to 14 g $\text{EtO}_2\text{CC!CCO}_2\text{Et}$ and 9.5 g $(\text{MeO})_2\text{POH}$ gave a vigorous reaction and distn of the mixture gave 3.2 g $[\text{CH}(\text{CO}_2\text{Et})(\text{PO}(\text{OMe})_2)]_2$, $b_3^{200-3^\circ}$, $n_D^{20} 1.4635$, $d_4^{20} 1.2715$, and 15.6 g fraction, $1670-200^\circ$, from which no individual substance could be fractionated. The structures of the diphosphonates listed above are not ascertained but appear probable.

(b) Addition of diethyl thiophosphite to ketones and aldehydes, by A N Pudovik and G A Zametaeva, published in Izvest Akad Nauk SSSR, Otdel Khim Nauk, 932-9 (1952).

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In the presence of EtONa, $(EtO)_2PSH$ forms an equilibrium mixture of EtOH and $(EtO)_2P(S)Na$, which is capable of addn to various double bonds, including that of the carbonyl structures. Addn of 8 g $(EtO)_2PSH$ (b_6 63°, n_D^{20} 1.4587, d_4^{20} 1.0763) to 4.4 g ethyldene-acetone, followed by dropwise addn of EtONa-EtOH led to vigorous reaction and distn of the mixture after 0.5 hr gave 6.2 g, (50.1%), $AcCH_2CHMeP(S)(OEt)_2$, b_{12}^{142-4} °, n_D^{20} 1.4638, d_4^{20} 1.0549, a greenish liquid with unpleasant odor. This (5 g) kept 5 days with 2.3 g PhMHNH₂ and 6 ml abs EtOH in a desiccator, then distn gave 1.5 g corresponding phenylhydrazone, b_9 238-40°, a red viscous liquid; the ester (1.5 g), 0.8 g semicarbazide-HCl in aq soln and 0.6 g AcONa treated with 5 ml EtOH, heated to boiling and cooled gave in 2-3 hrs the corresponding semicarbazone, m 124° (from EtOH). Addn of 15-20 drops EtONa-EtOH to 5.3 g $(EtO)_2PSH$ and 5 g benzalacetone similarly gave 4.6 g (46.5%) $AcCH_2CHPhP(S)(OEt)_2$, b_7 177-9°, n_D^{20} 1.5344, d_4^{20} 1.1462. Addn of 20 drops EtONa-EtOH to 6.85 g $(EtO)_2PSH$ and 5 g mesityl oxide, followed by 0.5 hr on a steam bath gave 8 g (74.1%) $AcCH_2C(Me)_2P(S)(OEt)_2$, b_{12}^{128-30} °, n_D^{20} 1.4731, d_4^{20} 1.0590; phenylhydrazone, b_{12}^{234-5} °, forms after 10 days at room temp with PhMHNH₂ in EtOH; semicarbazone, m 123° (from EtOH). Addn of 15 drops EtONa-EtOH to 5 g furfuralacetone and 6 g $(EtO)_2PSH$ similarly gave 5.1 g (48.7%) 1-furyl-1-(diethylthiophosphono)-3-butanone, b_7 164-6°, n_D^{20} 1.5025, d_4^{20} 1.1471. Addn of 25-30 drops EtONa-EtOH to 17 g Me_2CO and 4.8 g $(EtO)_2PSH$ caused but a mild reaction; after 2 hrs on a steam bath the mixture yielded 4 g (62.1%) $Me_2C(OH)P(S)(OEt)_2$, b_{10}^{107-9} °, n_D^{20} 1.4684, d_4^{20} 1.0735, whose EG group is determinable by Zarevitinov method. Addn of 20 drops EtONa-EtOH to 10 g $(EtO)_2PSH$ and 3.6 g acrolein stabilized with hydroquinone, with cooling, followed by neutralization with AcOH and distn, gave 6 g (46.2%) $CH_2=CHCH(OH)P(S)(OEt)_2$, b_{10}^{120-2} °, n_D^{20} 1.4828, d_4^{20} 1.1158; PhMHNH₂ in EtOH in 6 days gave no phenylhydrazone, and a similar neg result was secured with semicarbazide; quant bromination showed 1 double bond. EtONa-EtOH added to 4.4 g $(EtO)_2PSH$ and 2 g crotonaldehyde gave a vigorous reaction and distn of the product gave 2.4 g (43.7%) $MeCH=CHCH(OH)P(S)(OEt)_2$, b_3^{130-2} °, n_D^{20} 1.4846, d_4^{20} 1.1019. To 4 g $(EtO)_2PSH$ and 3.2 g furylacrolein in 6 ml abs EtOH was added EtONa-EtOH; the reaction was less vigorous than the preceding one; distn gave 2.8 g (46.1%) 1-hydroxy-3-furyl-1-(diethylthiophosphono)-2-propene, b_{10}^{101-2} °, n_D^{20} 1.5280, d_4^{20} 1.0785, m 25-6°. Addn of 20 drops EtONa-EtOH to 5 g $(EtO)_2PSH$ and 1.5 g AcH gave a vigorous reaction and

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after 24 hrs at room temp the mixture gave 4 g (62.3%) $\text{PrCH}(\text{OH})\text{P}(\text{S})(\text{OEt})_2$, b₁₂ 111-12°, n_D²⁰ 1.4721, d₄²⁰ 1.1029. Similar reaction with PhCHO gave 45.4% $\text{PrCH}(\text{OH})\text{P}(\text{S})(\text{OEt})_2$, b₇ 102-3°, n_D²⁰ 1.4781, d₄²⁰ 1.0925.

(c) New method of synthesis of esters of aminophosphonic acids, by A N Pudovik and M V Korchekina, published in Izvest Akad Nauk SSSR, Otdel. Khim Nauk 940-6 (1952).

(RO)₂POH add to derivs of benzalaniline in the presence of KOH catalyst yielding esters of aminophosphonic acids in good yields. To avoid ester exchange the KOH must have the same radical R as the dialkyl phosphite. The general procedure of addn of 15-20 drops satd RO₂-ROH to 3-4 g benzalaniline deriv and equimolar amount of (RO)₂POH, followed by one hour on a steam bath gave the products in crystalline form after several hours or days standing in an open dish; crystallization from EtOH gave the pure products listed below. With acetophenoneanil it was necessary to heat the mixture 1-2 hours at 150-80° to complete the reaction. The following esters were reported. p-iso- $\text{PrC}_6\text{H}_4\text{CH}(\text{NHPH})\text{PO}(\text{OMe})_2$, 67.7%, m 106-7°; di-Et analog, 76.6%, m 150°; p-MeC₆H₄CH(NHPH)PO(OMe)₂, 77.8%, m 121-2°; di-Et analog, 82.3%, m 66°; o-O₂NC₆H₄CH(NHPH)PO(OMe)₂, 77.2%, m 175.5-6.0°; di-Et analog, 87.7%, m 155°; n-O₂NC₆H₄CH(NHPH)PO(OMe)₂, 82.8%, m 130-1°; di-Et analog, 90.9%, m 93-4°; PhCH(PO(OEt)₂)NHC₆H₄Cl-p, 75.4%, m 111-13°; m-O₂NC₆H₄CH(PO(OEt)₂)-NHC₆H₄Me-m, 78.7%, m 129-30°; p-iso- $\text{PrC}_6\text{H}_4\text{CH}(\text{PO(OEt})_2)\text{NHC}_6\text{H}_4\text{Cl-p}$, 82.7%, m 119-9.5°; p-MeC₆H₄CH(PO(OEt)₂)NHC₆H₄Me-m, 88%, m 102-3°; p-iso- $\text{PrC}_6\text{H}_4\text{CH}(\text{PO(OEt})_2)\text{NHC}_6\text{H}_4\text{Me-o}$, 79.1%, m 115°; MeEtc(NHPH)PO(OEt)₂, 75%, m 106-8°; Et₂C(NHPH)PO(OEt)₂, 78.8%, m 119-20°. Reaction products with (RO)₂POH and o-hydroxybenzalaniline failed to crystallize; the reaction apparently failed to take place with benzo-phenoneanil, acetophenone-o-methylanil and the m-analog; at least, no crystalline products could be obtained. Reaction of (EtO)₂POH with benzalaniline was investigated in 0.725-1.45 M solns in the presence of 17.4% MeONa in MeOH at 70°; the titration of unreacted (EtO)₂POH with 0.5N NaOH in presence of phenolphthalein was used as the means of following the reaction. In abs EtOH the reaction failed to occur at low concns, while at high concns it ran its course too rapidly and with too much heat evolution for accurate detns of the rate. These results were obtained with EtOH dried over CaO, followed by Na. Use of EtOH that was additionally dried over Mg gave much better results. At 50° a

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1.45 M soln of the reagents (50 ml) with 0.5 ml MeONa soln added gave a straight line decrease of unreacted $(EtO)_2POH$ with some 25% completion in six hours; with 1 ml catalyst the reaction was 50% complete almost instantly after which it followed a logarithmic curve approaching 90% at six hours; with 3 ml catalyst the reaction was nearly instantaneous; with 0.725M soln at 30.4° the results are similar, very little reaction taking place with 2 ml catalyst, some 90% completion with 2.5 ml and instantaneous reaction with 3 ml. The results indicate extraordinary sensitivity of the reaction to traces of moisture, which destroys $(EtO)_2PONa$; this confirms the ionic chain mechanism of the addn reaction.

(d) Addition of dialkyl phosphites and their chlorides to α -oxides, by A N Pudovik and B E Ivanov of the Kazan State University, published in Izvest Akad Nauk SSSR, Otdel Khim Nauk, 947-55 (1952).

Passage of ethylene oxide (I) into Et_2O soln of $(EtO)_2PONa$, treatment with AcOH, filtration and distn gave largely the original ester and only a trace of product, b_5^{115-25} , along with much tar. Run at elevated temp the reaction gives but slightly improved yields. BF_3 and its adducts are the best catalysts for addn of dialkyl phosphites to olefin oxides. Heating 20 g $(EtO)_2POH$, 10 g I and 0.015 ml BF_3-Et_2O in a sealed tube eight hours at 130° gave after two distns 3.5 g $HOCH_2CH_2PO(OEt)_2$, b_8^{122-4} , $n_D^{20}1.4380$, $d_4^{20}1.0927$; at lower temp the reaction is very slow, at higher temp much destruction of the products occurs. Small amounts of concd H_2SO_4 give somewhat lower yields than does BF_3 . Heating 20 g $(MeO)_2POH$ with 12 g I and 0.015 ml BF_3-Et_2O eight hours at 130-5° in sealed tube gave 3 g $HOCH_2CH_2PO(OMe)_2$, b_6^{95-7} , $n_D^{20}1.4240$, $d_4^{20}1.1711$. $(iso-BuO)_2POH$ (15 g) and 7 g I with 0.015 ml Et_2O-BF_3 failed to react even at 160-70°; the di-Bu ester also gave negative results at 135°. To soln of 2.3 g Na in 13.8 g $(EtO)_2POH$ in 100 ml Et_2O was added 10.2 g $EtOCH_2CHCH_2O$, the mixture was refluxed three hours, treated with 7 ml AcOH, filtered, and distd yielding 3.5 g crude, or 1.7 g pure, $EtOCH_2CH(OH)CH_2PO(OEt)_2$, b_5^{115-16} , $d_4^{20}1.0831$, $n_D^{20}1.4385$. Reaction of 13.8 g $(EtO)_2POH$ with 10.2 g $EtOCH_2CHCH_2O$ and 0.05 ml BF_3-Et_2O in eight hours at 130-5° in sealed tube gave 3 g product, b_7^{137-9} , $d_4^{20}1.1023$, $n_D^{20}1.4432$, and 2.5 g product, b_7^{155-6} , $n_D^{20}1.4520$,

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$d_4^{20} 1.1745$; the former contained 13% P, the latter 15% P; it is believed that with BF_3 catalyst the reaction yields as one product di-Et β -hydroxy- β -ethoxyisopropylphosphonate. Heating 25 g $(\text{EtO})_2\text{POH}$ with 16 g cyclohexene oxide and 0.015 ml $\text{BF}_3\text{-Et}_2\text{O}$ in ampul eight hours at 140-50° gave 4.5 g di-Et β -hydroxy-cyclohexylphosphonate, $C_{10}\text{H}_{21}\text{O}_4\text{P}$, $b_7^{142-4^\circ}$, $d_4^{20} 1.0930$, $n_D^{20} 1.4620$. Passage of I into 35 g $(\text{EtO})_2\text{PCl}$ until 10 g wt gain was reached at 20-5°, followed by distn gave: 4 g $(\text{EtO})_3\text{P}$, $b_7^{46^\circ}$, $n_D^{20} 1.4158$, $d_4^{20} 0.9866$; 20 g $(\text{EtO})_2\text{POCH}_2\text{CH}_2\text{Cl}$, $b_5^{72-4^\circ}$, $n_D^{20} 1.4392$, $d_4^{20} 1.1038$; and 8 g $\text{EtOP}(\text{OCH}_2\text{CH}_2\text{Cl})_2$, $b_{15}^{125-8^\circ}$, $n_D^{20} 1.4609$, $d_4^{20} 1.2268$. (II) Heating 10 g II with 5.5 g EtBr in sealed tube five hours at 160° gave 7 g $\text{EtPO}(\text{OEt})(\text{OCH}_2\text{CH}_2\text{Cl})$, $b_7^{67-8^\circ}$, $d_4^{20} 1.0911$, $n_D^{20} 1.4168$. Addn of 10 g $(\text{EtO})_2\text{PCl}$ to Et_2O soln of $\text{MeCH}_2\text{CH}_2\text{CO}$ (unstated amount) with cooling gave 2.5 g $(\text{EtO})_3\text{P}$, and 5 g (5%) $(\text{EtO})_2\text{POCH}_2\text{CH}_2\text{MeCl}$, $b_{12}^{99^\circ}$, $n_D^{20} 1.4367$, $d_4^{20} 1.0633$, and 4 g $\text{EtOP}(\text{OCH}_2\text{CH}_2\text{MeCl})_2$, $b_5^{130-2^\circ}$, $n_D^{20} 1.4500$, $d_4^{20} 1.0931$. Addn of 6.5 g $(\text{EtO})_2\text{PCl}$ to 4 g cyclohexene oxide gave an exothermic reaction and on distn there was obtained after two fractionations 3 g diethyl 2-chloro-cyclohexyl phosphite, $b_{17}^{130-2^\circ}$, $n_D^{20} 1.4650$, $d_4^{20} 1.1082$. Passage of I (5.5 g weight gain) into 15 g $\text{CH}_2\text{CH}_2\text{OPClO}$ with cooling gave on distn 19 g $\text{CH}_2\text{CH}_2\text{OP}(\text{OCH}_2\text{CH}_2\text{Cl})_2$, $b_{10}^{82-3^\circ}$, $d_4^{20} 1.3185$, $n_D^{20} 1.4760$.

(e) Reaction of phosphoncetylation and diene synthesis with vinylphosphonic esters, by A N Fudovik and M G Imayev of the Kazan State University, published in Izvest Akad Nauk SSSR, Otdel Khim Nauk, 916-22 (1952).

Attempts to obtain $\text{BrCH}_2\text{CH}_2\text{P}(\text{O})(\text{OMe})_2$ from $(\text{MeO})_3\text{P}$ and $(\text{CH}_2\text{Br})_2$ failed since the MeBr evolved caused immediate isomerization of $(\text{MeO})_3\text{P}$. However, when 150 g $(\text{CH}_2\text{Br})_2$ was added dropwise to 30 g $(\text{BuO})_3\text{P}$ preheated to 170° and heated 3.5 hrs at 170-90° with evolution of BuBr there was obtained 2 g $\text{BuP}(\text{O})(\text{OBu})_2$ and 19.8 g $\text{BrCH}_2\text{CH}_2\text{P}(\text{O})(\text{OBu})_2$, contaminated with some of the previous ester; this product $b_5^{146-7^\circ}$, $n_D^{20} 1.4485$, $d_4^{20} 1.1400$; also was obtained 2.5 g $(\text{BuO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OBu})_2$, $b_7^{207-10^\circ}$, $n_D^{20} 1.4402$, $d_4^{20} 1.0240$. If the order of addn is reversed the reaction failed to take place owing to too low b pt of $(\text{CH}_2\text{Br})_2$. To 15 g Br deriv in 100 ml EtOH was added dropwise 2.5 g KOH in EtOH with ice-cooling; distn after filtration gave 7 g $\text{CH}_2\text{:CHP}(\text{O})(\text{OBu})_2$, $b_5^{115-6^\circ}$, $n_D^{20} 1.4372$, $d_4^{20} 0.9810$, (75%), (I). Heating 40.5 g $(\text{MeO})_3\text{P}$ with 100 g $(\text{CH}_2\text{Br})_2$ to 150°

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gave much MeP₂ (10 g) and distn gave 50 g (CH₂Br)₂, 15 g (MeO)₃P and 25 g MeP(O)-
(OMe)₂, b₈ 66-8°, n_D²⁰ 1.4135, d₄ 1.1684, as well as some tarry material. To 6 g
CH₂:CHP(O)(OEt)₂, (II), in 42 g abs EtOH and 0.3 g EtONa, was added H₂S until the
soln was satd at room temp; after 24 hrs distn gave 3 g unreacted II and 2.5 g
HSCH₂CH₂P(O)(OEt)₂, b₃ 95-6°, n_D²⁰ 1.4210, d₄ 1.0392; 75% yield is achieved if the
reaction is run at 100° in sealed tube 15 hrs. Heating 5 g II with 4 g EtSH
and 0.3 g EtONa in sealed tube 18 hrs at 100° gave 3.5 g EtSCH₂CH₂P(O)(OEt)₂,
b₄ 96°, n_D²⁰ 1.4265, d₄ 1.0406. Heating 5 g I with 4.5 g EtSH and a little BuONa
in sealed tube at 100° gave 3.1 g EtSCH₂CH₂P(O)(OBu)₂, b₇ 165-7°, n_D²⁰ 1.4580,
d₄ 1.0109 (78%). Heating 7 g II, 10 g piperylene and 0.1 g hydroquinone in
sealed tube 25 hrs at 170-80° gave 3 g piperylene dimer, 2.5 g II and 3.5 g,
63.5%, di-Et 2-methyl- Δ^3 -cyclo-hexenephosphonate, b₃ 118-19°, n_D²⁰ 1.4488, d₄ 1.0166.
Similar reaction with I at 190-200° gave 65.2% di-Bu ester analog, b₃ 155-6°,
n_D²⁰ 1.4801, d₄ 1.0379. Heating 3 g II and 10 g 2,4-hexadiene with a little hydro-
quinone in sealed tube 25 hrs at 250-70° gave 2 g (44%), di-Et 2,5-dimethyl- Δ^3 -
cyclohexenephosphonate, b₇ 125-7°, n_D²⁰ 1.4505. Similar reaction with I at 270-90°
gave 36.4% di-Bu ester analog, b₃ 154-6°, n_D²⁰ 1.4710, d₄ 1.0042. The reaction
products from piperylene were single substances, indicating that the addn occurs
in accord with the electronic theory with development of neg center at the ter-
minal C atom of piperylene and pos center at the terminal atom of I or II.

(f) New method of synthesis of esters of phosphonic and thiophosphonic acids,
5, Addition of esters of phenyl- and alkylphosphonous acids to esters of metha-
crylic and acrylic acids, by A N Pudcvik and D Kh Yarmukhametova of the A E
Arbusov Chem Institute at Kazan, published in Izvest Akad Nauk SSSR, Otdel Khim
Nauk, 902-7 (1952).

To 15 g abs MeOH was gradually added 14.6 g PhPCl₂, the resulting HCl was re-
moved in vacuo over 3-4 hrs and the residue on distn gave 8.4 g (66%) PhP(OMe)OH,
b₁ 91-3°, n_D²⁰ 1.5322, d₄ 1.1770. PhPCl₂ (25 g) and 20 g abs EtOH gave 20 g (84%)
PhP(OEt)OH, b₁ 94-5°, n_D²⁰ 1.5231, d₄ 1.1291. PhPCl₂ (11.3 g) and 11.3 g abs iso-
PrOH gave 70% PhP(OCHMe₂)OH, b₁ 106-7°, n_D²⁰ 1.5111, d₄ 1.0922; similarly 14.8 g
PhPCl₂ and 18.5 g iso-BuOH gave 88% PhP(OCH₂CHMe₂)OH, b₁ 112-13°, n_D²⁰ 1.5081,
d₄ 1.0675; 10.7 g PhPCl₂ and 18.3 g C₆H₁₃OH gave 60% PhP(OCH₂H₁₃)OH; b₁ 139°,

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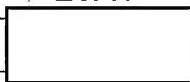
n_D^{20} 1.5030, d_4^{20} 1.0388; 10 g PhPCl₂ and 19 g C₇H₁₅OH gave 80% PhP(OC₇H₁₅)OH, $b_1^{150^\circ}$, n_D^{20} 1.4996, d_4^{20} 1.0187; 8.8 g PhPCl₂ and 19.2 g C₈H₁₇OH gave 78% PhP(OC₈H₁₇)OH, $b_1^{155^\circ}$, n_D^{20} 1.4982, d_4^{20} 1.0079; 10 g PhPCl₂ and 24 g C₉H₁₉OH gave 57% PhP(OC₉H₁₉)OH, $b_1^{158-60^\circ}$, n_D^{20} 1.4900, d_4^{20} 0.9843. Addn of these esters to acrylates and methacrylates gave products with sharp b pts without any evidence of ester exchange, even when EtONa was used as catalyst. Thus, to 7 g PhP(OEt)OH and 4.1 g CH₂:CMe-CO₂Me was added 4-5 drops satd EtOH-EtONa and after the exothermic reaction, the mixture gave on distn 8 g MeO₂CCHMeCH₂P(Ph)(O)OEt, $b_0.5^{151-3^\circ}$, n_D^{20} 1.5064, d_4^{20} 1.1390, 72%. Similarly CH₂:CHCO₂Me gave 76% MeO₂CCH₂CH₂PPh(O)OEt, $b_2^{159-60^\circ}$, n_D^{20} 1.5081, d_4^{20} 1.1619; use of CH₂:CMeCO₂Et gave 82% EtO₂CCHMeCH₂PPh(O)OEt, $b_2^{159-60^\circ}$, n_D^{20} 1.4992, d_4^{20} 1.1140; use of CH₂:CMeCO₂Pr gave 74% PrO₂CCHMeCH₂PPh(O)OEt, $b_2^{159-60^\circ}$, n_D^{20} 1.4962, d_4^{20} 1.0988. Similarly, 6.1 g PhP(OCH₂CHMe₂)OH and 3 g CH₂:CMeCO₂Me gave 45% MeO₂CCHMeCH₂PPh(O)OCH₂CHMe₂, $b_1^{156^\circ}$, n_D^{20} 1.4965, d_4^{20} 1.0962; similarly was obtained 40% MeO₂CCHMeCH₂PPh(O)OC₆H₁₃, $b_1^{176-7^\circ}$, n_D^{20} 1.4908, d_4^{20} 1.0589. Reactions of RP(OR)OH, where R= alkyl group with unsatd esters gave mixtures with wide b pts unless the R of RONa catalyst was identical with the R of the esters used. With this precaution, 4 g EtP(OBu)OH and 3.8 g CH₂:CMeCO₂Bu gave 75% BuO₂CCHMeCH₂PEt(O)OBu, $b_1^{137-8^\circ}$, n_D^{20} 1.4450, d_4^{20} 1.0025, while CH₂:CH-CO₂Bu gave 74% BuO₂CCH₂CH₂PEt(O)OBu, $b_1^{141^\circ}$, n_D^{20} 1.4490, d_4^{20} 1.0146. In all esters of type PhP(OR)OH the found value of molecular refraction exceeded the calcd values by 1.1-1.5 units indicating a constitutive effect of Ph group on refractivity of P.

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